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THERMO CHEMICAL ANALYSIS OF THE REOXIDATION IN THE SAND MOULDS.

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ABSTRACT: Evolution of atmosphere of the mould cavity when pouring the cast iron has been analyzed. It was find that in dry sand mold the cavity is filled by air throughout the casting time. In green sand the air is removed by the water vapor the hydrogen or carbon oxides formed in contact with the liquid metal. The theoretical results have been confirmed experimentally.

KEY WORDS: reoxidation, mould atmosphere; thermo chemical analysis.

1. INTRODUCTION.

In the numerous papers it was stated that during casting of iron in the green sand mould the surface of metal is oxidized [1,2,3,4] forming the defects like surface porosity, pinholes etc It was experimentally proved that when the metal fills the mould cavity the partial pressure of oxygen quickly decreases especially when the sand is prepared with the addition of the coal dust. [3,5]. In general opinion, when pouring the cast iron in presence of coal dust, the mould atmosphere becomes reducing . When the steel is cast in the green sand mould the results are different. For the laboratory tests and industrial castings it was found that the drop of partial pressure of oxygen in the green sand mould is independent of the presence of coal dust in the moulding sand. Method of testing has been presented in the former papers [3,5], the results are presented in the Figure 1

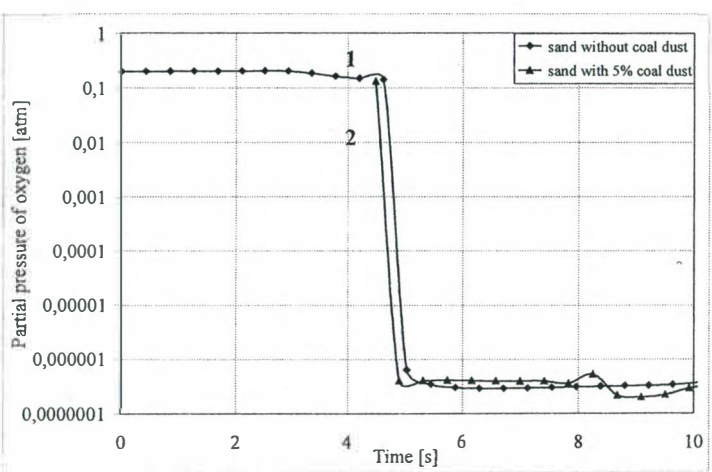

Fig.1. Evolution of the partial pressure of oxygen in the gas removed from the green sand mould filled with cast steel.

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Experimental evaluation of reoxidation effects is rather difficult. The rise of the oxygen activity in alloy is negligible [4,5]. The reoxidation is limited to the surface layer when the oxides forms and the time of the mould filling is too short for the diffusion to the bulk metal. Also the measure of the total oxygen by extraction gives a doubtful results. They are averaged for a large volume. For this reason authors decided to study the probability of the oxidation and reduction reactions between the gas formed in the mould, initial atmosphere in mould cavity and the liquid iron.

2. THERMOCHEMICAL ANALISYS OF THE REOXYDATION.

2.1 Dry sand mould

At the initial moment of pouring the mould cavity is filled by air and partial pressure of the oxygen $Po_2 = 0.21$. The rest is nitrogen . Short time of pouring eliminates the possibility of its transfer to the metal. The atmosphere character is determined by reaction :

$$\{½\ O_2\} = [O] \qquad [1]$$

It's free Gibb's energy is equal to[6]:

$$\Delta G^\circ = -123720 - 0.5031\ T\ J/mol.$$

Figure 2 presents calculated oxygen activity for the equilibrium with iron saturated with oxygen.

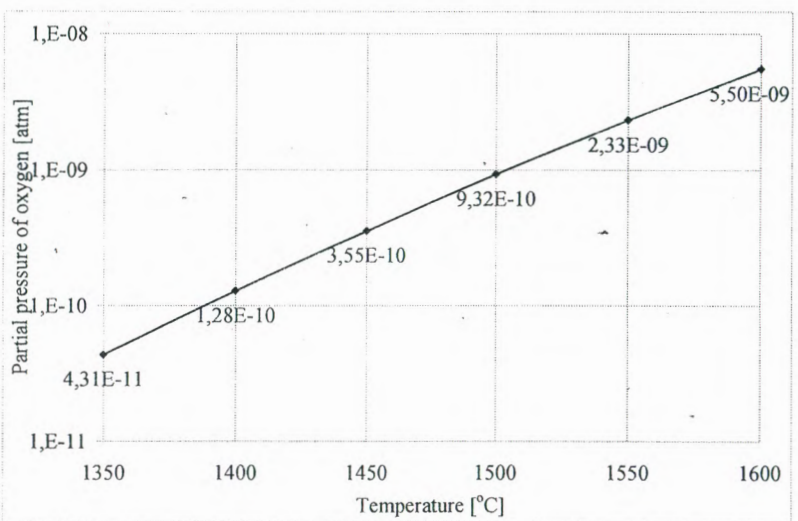

Fig. 2.Oxygen activity for the equilibrium for iron saturated with oxygen.

Results of calculation are much lower then experimentally measured in green sand mould (Fig.1) . It indicates that forming of reducing atmosphere is improbable. The reoxidation can be only impended by limiting the time of reaction or partial pressure of oxygen. Figure 3 presents the evolution of Po_2 during filling the dry sand mould with cast iron. It rests on the constans level. A little drop may be observe because a part of oxygen is consumed for oxidations of iron or more probably oxidation of other cast iron elements: aluminum, silicon or even carbon. Addition of the coal dust or other reducing elements to the dry sand can ameliorated the casting surface quality, rising the interfacial energy mould-metal. The lack of oxygen in the sand excludes the possibility of carbon oxidation in the bulk sand. For the reaction :

$$C+\{O_2\} = \{CO_2\} \qquad (2)$$

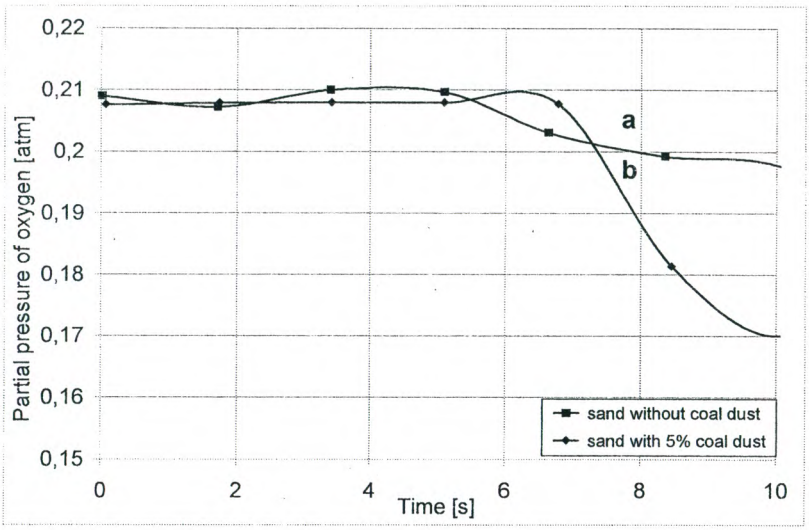

Fig. 3. Evolution of the partial pressure of oxygen during casting the iron in dry sand mould.

the nucleation of gas bubbles and then the high supersaturation is necessary The oxidation is possible only at the surface of cavity. The quantity of carbon dioxide formed is too limited to influence the mould atmosphere. It is confirmed experimentally. Results are presented in the Figure 3 The partial pressure of oxygen doesn't change during filling the mould

2.2. Green sand mould without the coal dust addition.

In the green sand mould the water steam forms in condensation zone. For nucleation the pressure of steam must attain 100 kPa. Transport through the dried layer is isobaric and the raise of temperature increases the volume of steam. In the green sand mould with 5% humidity from 1 G of the sand is evacuated 0.05 G of water. After evaporating and heating to 1000 °C it's volume attains $3.61.10^{-4}$ m^3. During filling the mould with cast iron or steel the steam fulfils practically all free volume of the mould. It results the drop of partial pressure of oxygen. In the gas leaving the mould it rests only 10^{-8} atm. Evolution of the partial pressure of oxygen is presented in the Figure 4 The water steam oxidizes the liquid iron because for the reaction:

$$\{H_20\} + [Fe] = (FeO) + \{H_2\} \qquad (3)$$

the Gibbs free energy is very negative and equals [7]:

$\Delta G^o = -79960+78.53T$ J/mol

The oxidation causes the sudden rise of the partial pressure of hydrogen especially at the temperature of liquid steel. This pressure is nearly in equilibrium with iron saturated with hydrogen. It is presented in the table 1

Hydrogen is partly absorbed by metal, the rest is evacuated from mould, burning outside in contact with atmosphere. The oxygen from reduction of the water steam forms the iron oxide The pieces cast in green sand are particularly endangered by reoxidation. The oxidizing result however of contact with water steam and not the free oxygen because its evacuated from the mould just at the beginning of pouring. The calculated pressure of hydrogen can be much more dangerous for casting surface, particularly for the long pouring time. This opinion is confirmed by foundry practice. Frequently the pinholes appears in castings produced in green sand moulds, especially for alloys with high concentration of strong deoxidizers like aluminum or magnesium. They react with steam much easier then iron and the absorption of hydrogen is quicker.

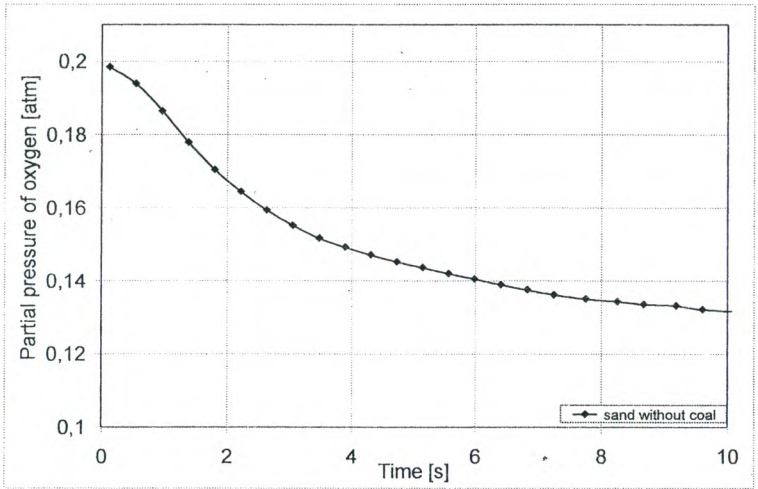

Fig.4. Evolution of the partial pressure of oxygen during pouring the cast iron in the green sand mould.

Table 1. Partial pressure of hydrogen in equilibria with water steam and liquid iron.

Temperature [C]	Partial pressure of hydrogen [bars]	Concentration of hydrogen in iron [ppm].
1350	0.971	19.00
1400	0.976	20.49
1450	0.980	21.98
1500	0.983	23.48
1550	0.985	24.98
1600	0.987	26.48

Green sand mould with the coal dust.

The water steam formed in condensation zone flows throughout the dry sand rich in coal dust and oxidizes the carbon:

$$2\{H_2O\} + C = 2\{H_2\} + \{CO_2\} \quad (4)$$

Gibbs free energy is equal to [7]:

$\Delta G^0 = 108700\text{-}116.57\ T$ J/mol

The pressure of steam equals 1 atm and the equilibrium pressure of the formed carbon dioxide can be calculated from equation. Figure 5 present this pressure for initial partial pressure of hydrogen 10^{-5} atm. Such a pressure is probable because at the temperature of the sand the steam dissociation rests negligible.

The rise of partial pressure of CO_2 is especially observed in regions where the temperature is higher then 350°C. C. Presented values are never obtained because short time of process and limited carbon content. The true concentration depends on the kinetic factors and have to be verified experimentally. It can be supposed that the mixture CO_2 –H_2O penetrates the mould cavity, replacing former air atmosphere. The partial pressure of oxygen drops to traces. It was confirmed experimentally as well for cast iron as for steel. The result of experiment is presented in the figure 6. In spite of heating the gas the reduction of carbon dioxide to monoxide is improbable. Reduction appears at the surface of liquid alloy: :

$[Fe]+\{CO_2\} = (FeO) +\{CO\}$ (5)

$\Delta G^o = -298679+175.52T$ J/mol [7]

Partial pressure of the carbon monoxide raises. It is presented in the Table 2.

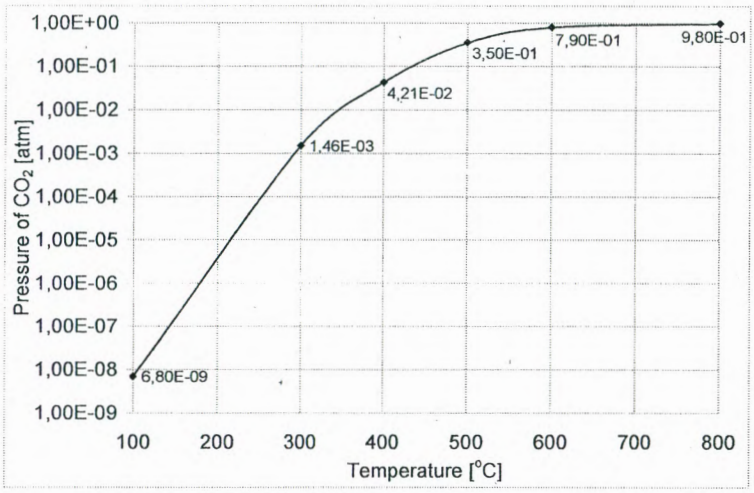

Fig. 5. Partial pressure of the carbon dioxide formed by reaction of water steam with carbon dust in the dried layer of mould.

Table 2 partial pressure of CO in equilibrium with carbon dioxide

Temperature °C	Partial pressure of CO_2			
	0.2	0.4	0.6	1
1200	0.00102	0.0041	0.0061	0.0102
1400	0.00329	0.0131	0.0197	0.0296
1600	0.00823	0.0339	0.0296	0.0741

More intensive is the reduction of water steam:

$\{H_2O\}+ [Fe] = \{H_2\} + (FeO)$ (6)

Even for the initial pressure of H_2O equals to 0.1atm ,at 1200°C presuure of hydrogen attains 0.75.

3. RESULTS

During casting the oxidation of ferrous alloys through oxygen is possible only in dried sand moulds. Even the addition of coal dust cannot change the initial air atmosphere. The formation of carbon oxide is possible only at the surface of mould cavity. In the green sand mould the water steam formed in condensation zone is transported to mould cavity and heated , but even at 700 °C no dissociation is possible. The steam fills the cavity eliminating former air atmosphere. Partial pressure of oxygen drops to 10^{-8} to 10^{-6} atm. Water steam reacts with liquid metal particularly with steel. In the zone of contact pressure of hydrogen is nearby the equilibrium with saturated alloy. It's transfer to the bulk metal is limited only by the short time of contact. When the coal dust id added to the green sand the steam promotes the

nucleation of the CO_2 bubbles in the dried layer. In equilibrium state nearly all steam is reduced, but the process of reduction depends on kinetic factors and the results cannot be provided from thermo chemical considerations. In effect the cavity is filled by the mixture of H_2O and CO_2.Rise of CO_2 fraction in the gas lowers the reduction of the water steam and the absorption of hydrogen in liquid metal. Formation of lustrous carbon in green sand mould and it's morphology suggest that certain hydrocarbons must forms during casting. As the nature of this hydrocarbons not known, the probability of formation cannot be evaluated. The partial oxygen pressure in the gas carried away from mould filled with cast iron is lower then for sand mould without coal dust. In case of steel casting, process of the formation of new mould atmosphere is so quick that no difference is observed

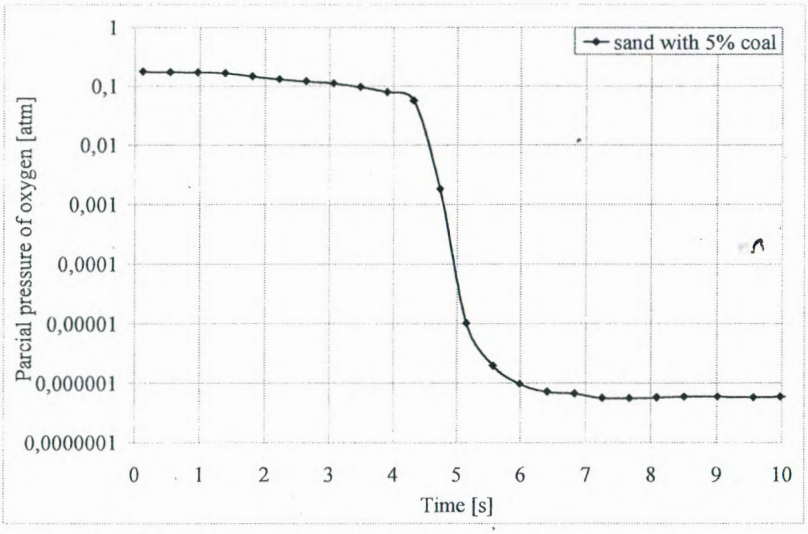

Fig.6.Evolution of the partial pressure of oxygen during pouring the cast iron in the green sand mould with 5% of coal dust.

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